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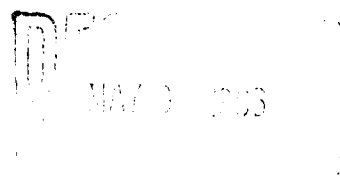
AFRPL-TR-65-232

**(U) MASS SPECTROMETRY OF CORROSIVE
OXIDIZERS AND XENON COMPOUNDS**

TECHNICAL REPORT AFRPL-TR-65-232

BERGE B. GOSHGARIAN

DECEMBER 1965



**AIR FORCE ROCKET PROPULSION LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
AIR FORCE SYSTEMS COMMAND
UNITED STATES AIR FORCE
EDWARDS, CALIFORNIA**

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FOREWORD

This report covers study conducted under Project 314802, Task 314802802, corrosive gas analysis phase. The research was conducted from May 1965 to July 1965.

The task was conducted by the Propellant Division, Chemical Branch, Air Force Rocket Propulsion Laboratory, Edwards, California.

This report has been reviewed and approved.



ELWOOD M. DOUTHETT

Colonel, USAF

Commander, Air Force Rocket Propulsion Laboratory

(U) ABSTRACT

A mass spectrometric study of reactive and corrosive oxidizers was successfully accomplished using a double-focusing mass spectrometer with a monel-Teflon sample introduction manifold. Reproducible spectra for compound "A", bromine pentafluoride, iodine pentafluoride, xenon tetrafluoride, xenon hexafluoride, oxygen difluoride, and fluorine were obtained with little difficulty after passivation of the manifold. Reaction products of the rhenium filament with oxygen difluoride, the passivation procedure, and the spectra of corrosive gases studied are discussed.

TABLE OF CONTENTS

<u>Section</u>	<u>Page</u>
1. INTRODUCTION	1
2. EXPERIMENTAL PROCEDURES	1
3. RESULTS AND DISCUSSION	4
4. CONCLUSIONS	14
REFERENCES	15
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LIST OF FIGURES

<u>Figure No.</u>	<u>Title</u>	<u>Page</u>
1	Corrosive Gas Mass Spectrometer Manifold	3
2	Rhenium Filament Reaction Products (RE + OF ₂).	6
3	Chlorine Pentafluoride (30 μ a 50 ev)	8
4	Bromine Pentafluoride (30 μ a 50 ev)	9
5	Iodine Pentafluoride (30 μ a 50 ev)	10
6	Xenon Tetrafluoride (30 μ a 50 ev)	11
7	Xenon Hexafluoride (30 μ a 50 ev)	12

LIST OF TABLES

<u>Table</u>		
I	Fluorine Pre- and Post-Passivation Spectra	5

(U) MASS SPECTROMETRY OF CORROSIVE OXIDIZERS AND XENON COMPOUNDS

1. INTRODUCTION.

(U) The identification of corrosive gas compounds and of impurities in these compounds requires special analytical procedures. The use of a mass spectrometer is particularly desirable since the molecular weight of (as well as the impurities in) the corrosive gas compounds can be obtained. Special handling systems have to be built to introduce these corrosive gases to the mass spectrometer ion source.

(U) Monel and nickel are the best readily available materials for corrosive gas handling manifolds due to their ability to form tenacious passive coatings with fluorinated gases, and further non-reactivity. Teflon is useful for gasketing and valve seats because of its non-reactivity with low pressure halogens. The elimination of any glass in the introduction manifold is desirable to avoid the formation of silicon tetrafluoride from reaction of fluorinated gases with silicon dioxide.

(U) This study was undertaken to demonstrate the capability of a double-focusing high resolution mass spectrometer equipped with a monel-Teflon introduction manifold for the analysis of corrosive compounds, and to elaborate the probable modes of molecular decomposition of these compounds upon electron impact.

2. EXPERIMENTAL PROCEDURES.

(U) A Mattauch-Herzog type double-focusing mass spectrometer manufactured by Consolidated Electrodynamics Corporation was used in this study. Ions produced from sample gas molecule bombardment by 50-volt electrons were accelerated through 8 kv and double-focused by tandem electric and magnetic fields.

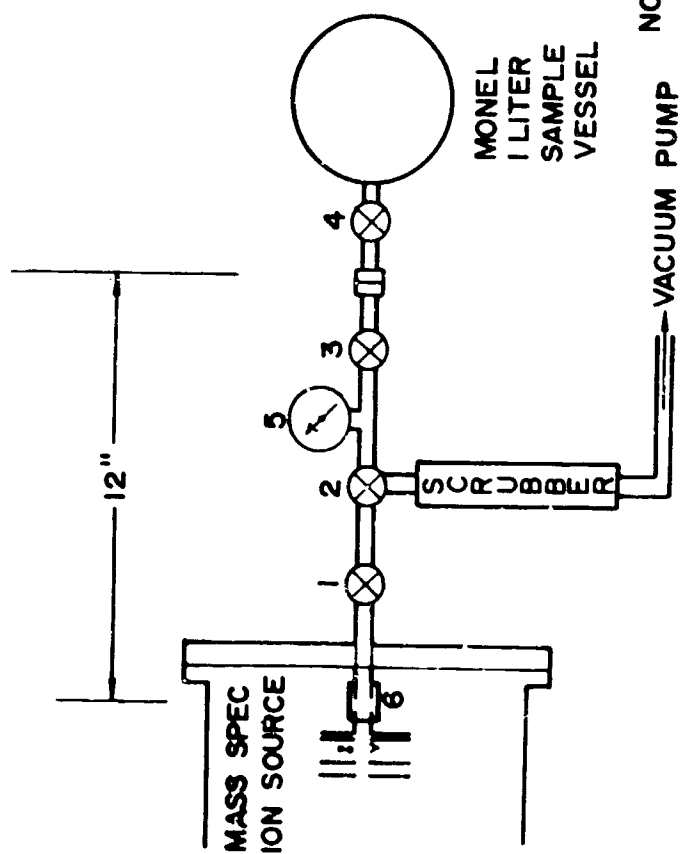
(U) Scanning of the spectrum was accomplished by varying the magnetic field strength, and detection of the ions was done with a 17-stage electron multiplier. An ion signal of approximately 5×10^{-13} amps at the beam monitor, which collected approximately one-fourth of the ion beam, was maintained throughout a scan. A minimum of five spectra per sample was obtained, and the average of peak height intensities was taken for the patterns presented.

(U) Pressures in the unheated source were maintained below 10^{-6} torr during scans using a 115 l/sec polyphenylether fluid vapor pump fitted with a liquid nitrogen trap. Even at the average source pressures of 5×10^{-7} torr, and trap current of 30 μ amps, the rhenium filament lasted only 100 hours. Inspection of the burned filament showed that the rhenium had been extensively eroded. All corrosive gas spectra obtained contained lines corresponding to rhenium-oxidizer reaction products.

(U) The original glass gas introduction system on the instrument was replaced with a monel-Teflon manifold. The valves and connectors were monel, and one valve seat and gaskets were Teflon. The manifold is shown in Figure 1. The $\frac{1}{4}$ -inch-diameter monel tubing extended to within $\frac{1}{4}$ inch of the ion source inlet tube, and the connection between the tubes was made with a Teflon tube sleeve. No glass was in contact with the sample gases to preclude the possibility of reactions to form silicon tetrafluoride.

(U) The monel-Teflon manifold was initially passivated with the corrosive gas under investigation for 12 hours prior to the study. After the passivation procedure, the gas in the manifold was pumped through a charcoal-potassium hydroxide scrubber until the manifold pressure was less than 1 micron. A fresh gas sample was then introduced to 700 torr manifold pressure or sample vapor pressure, and the metering valve regulated so that the ion source pressure did not exceed 1×10^{-6} torr. Spectra were obtained when the source pressure stabilized.

(U) Fluorine gas at 700 torr was initially used to passivate the manifold. Spectra were obtained 2 hours after the initial fluorine gas introduction. The fluorine was pumped out after 12 hours, and a new



NOTES

1. HOKE M1197 MONEL-TEFLON SEAT
BELLOWS VALVE
2. HOKE 415A & 3-WAY MONEL-BELLOWS
VALVE
- 3.) HOKE 413A MONEL BELLOWS VALVE
- 4.)
5. WALLACE & TIEMAN
0-800mm GAUGE
6. TEFLON TUBE SLEEVE

(U) Figure 1 Corrosive Gas Mass Spectrometer Manifold

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sample of fluorine gas introduced. Spectra of the new sample, after remaining 2 hours in the manifold, were also obtained, and an average of the spectra is compared, in Table I, with that for the initial fluorine passivation.

(C) The chlorine pentafluoride, designated Compound "A", was obtained from Rocketdyne, a Division of North American Aviation, and the bromine pentafluoride and iodine pentafluoride from the Matheson Company. The oxygen difluoride and fluorine were obtained from the Allied Chemical Company, and the xenon tetrafluoride and xenon pentafluoride were prepared at the Air Force Rocket Propulsion Laboratory, using methods described by Chernick (1) and Cady (2).

3. RESULTS AND DISCUSSION.

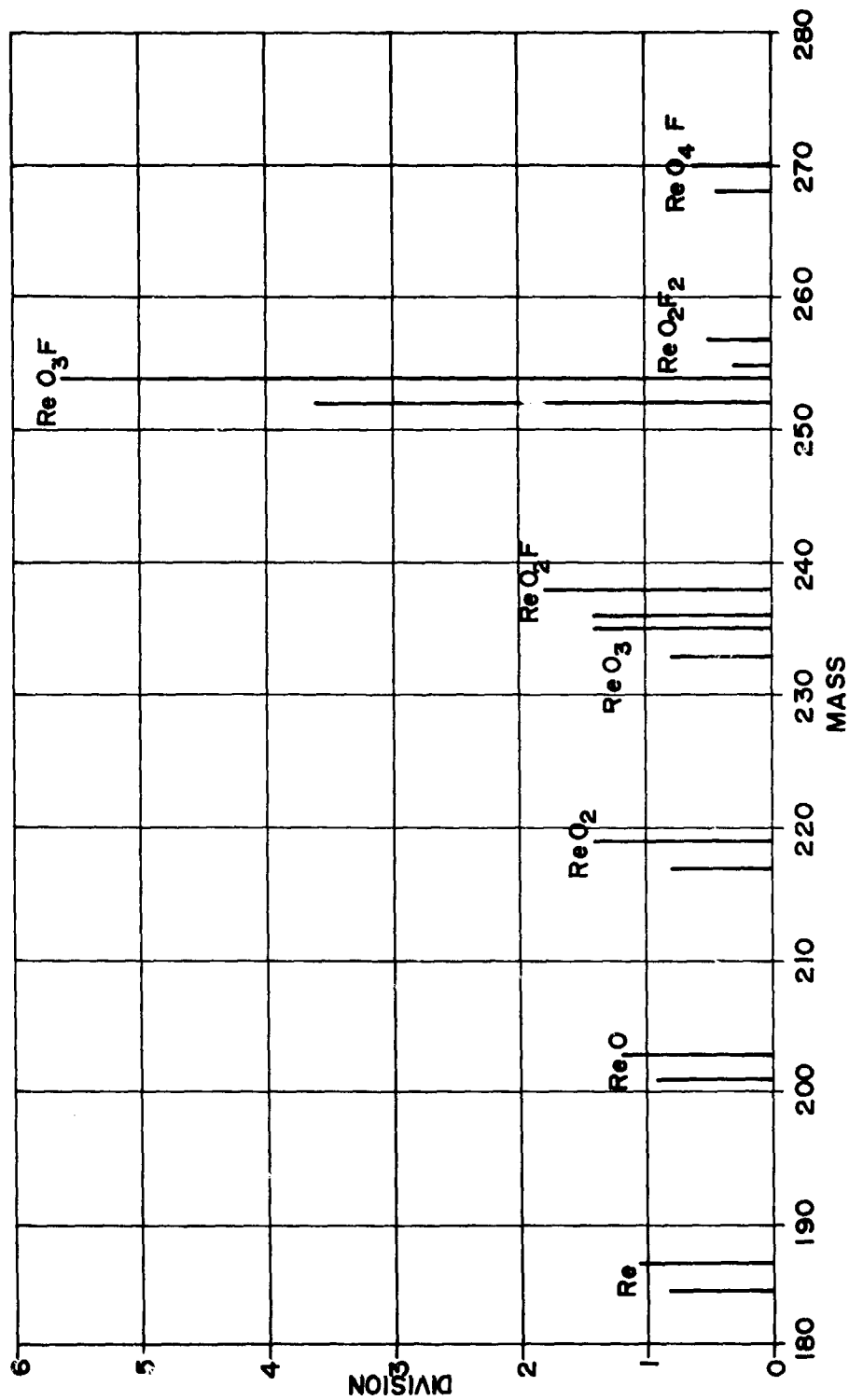
(U) The exclusive use of monel and Teflon in the sample introduction manifold proved very satisfactory. Passivation of the manifold with fluorine, and periodic analysis of the gas in the manifold, showed that the fluorine was reacting with either surface contamination or materials within the monel surface. The manifold was thoroughly cleaned and dried prior to fluorine introduction; therefore, it is highly likely that the observed molecular ions in the pre-passivation gas sample, Table I, originated from fluorine reacting with materials on the surface of the monel. Mass spectral analysis of gases in the manifold during passivation can be very useful in determining the completion of the passivation.

(U) All corrosive gas spectra displayed peaks corresponding to rhenium filament-oxidizer reaction products. The spectrum of oxygen difluoride-rhenium reaction products is shown in Figure 2.

(U) The ReO_3F^+ ion is the most abundant in the spectrum. Since the +7 oxidation state of rhenium is the most stable, the ReO_3F^+ ion probably originates from the ReO_3F parent molecule. The isotope peaks at m/e 268 and 270, are identified as the parent ion ReO_3OF^+ and not ReO_4F^+ . This assignment is made because in ReO_3OF^+ the rhenium is

4
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(U) Figure 2. Rhenium Filament Reaction Products (Re + OF₂)

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in its stable +7 state, while in order for ReO_4F^+ to exist, rhenium would have to exist in an unlikely +9 state.

(U) One further parent molecular ion, ReO_2F_2^+ , is observed in the spectrum. This ion peak is small because the rhenium in this molecule must exist in the unstable +6 oxidation state.

(U) The most probable compounds formed in the reaction of oxygen difluoride with the rhenium filament are, therefore, ReO_3F , ReO_3OF , and ReO_2F_2 .

(C) The spectra for chlorine pentafluoride, bromine pentafluoride, iodine pentafluoride, xenon tetrafluoride and xenon hexafluoride are shown in Figures 3 to 7.

(C) As observed, the parent molecular ions for the interhalogens increase in stability as the cation halogen increases in atomic weight. The increasing polarizability of the heavier halogen cations of bromine and iodine and the increased ease of electron removal from the parent molecule by electron bombardment account for this observation.

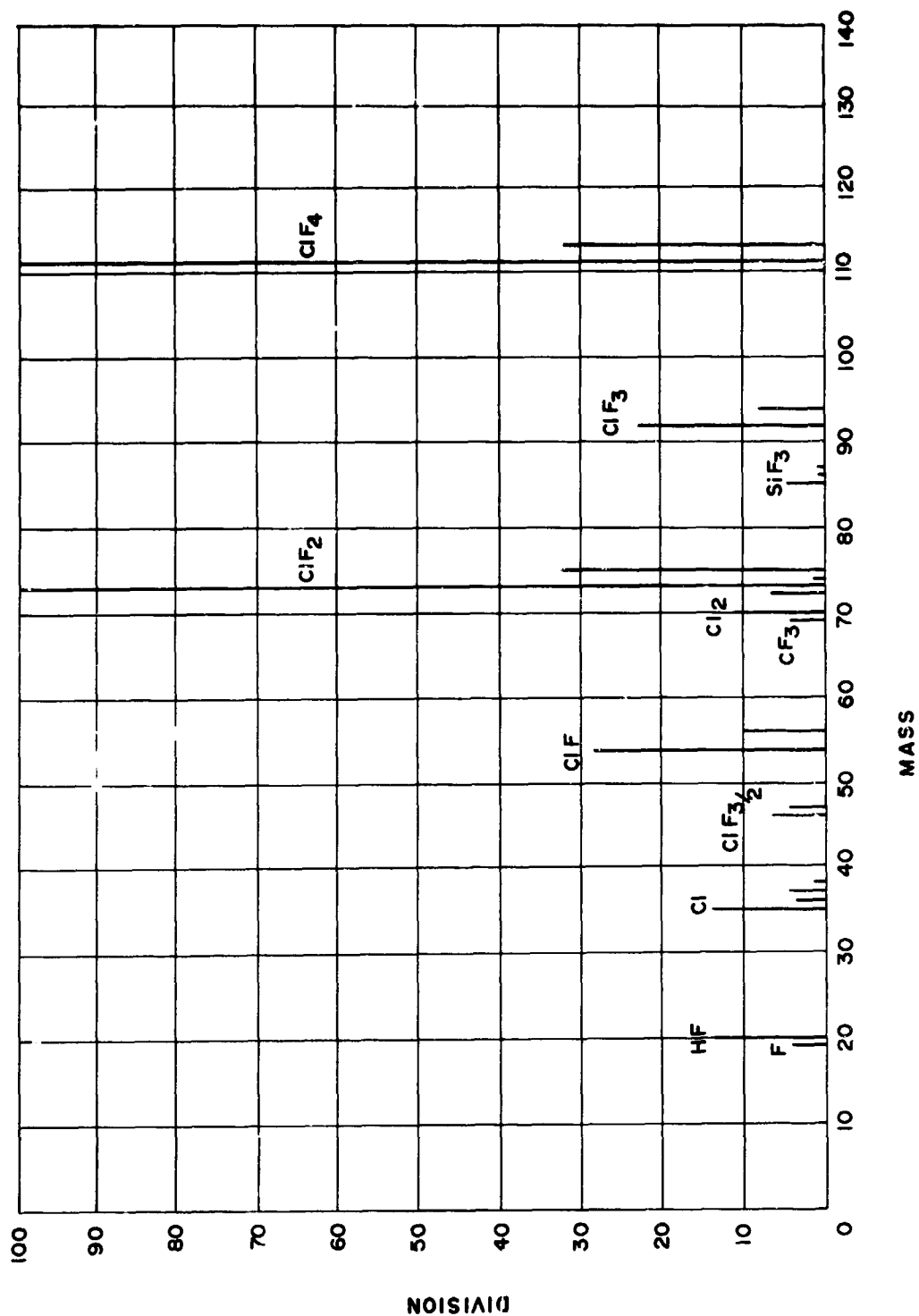
(C) The most intense molecule ion in the interhalogen spectra corresponds with the parent molecule minus a fluorine anion. The XF_4^+ ion has an even number of electrons; consequently, it is a stable specie. The XF_2^+ ion likewise has an even number of electrons, and is the second most stable ion, especially in the case of ClF_2^+ and, somewhat, in BrF_2^+ .

(U) Peaks at mass 158, 160 and 162 in the bromine pentafluoride spectrum were identified as free bromine in the sample. Analysis of the sample by nuclear magnetic resonance spectroscopy also indicated free bromine.

(C) The ion peaks, HF^+ , Cl_2^+ , and SiF_3^+ , in the chlorine pentafluoride spectra were reproducible and directly related to the chlorine pentafluoride concentration. Since these ions were in negligible concentration after passivation of the manifold, they must be present in the chlorine pentafluoride sample. Infrared analysis did show hydrogen fluoride and silicon tetrafluoride as impurities in the chlorine pentafluoride.

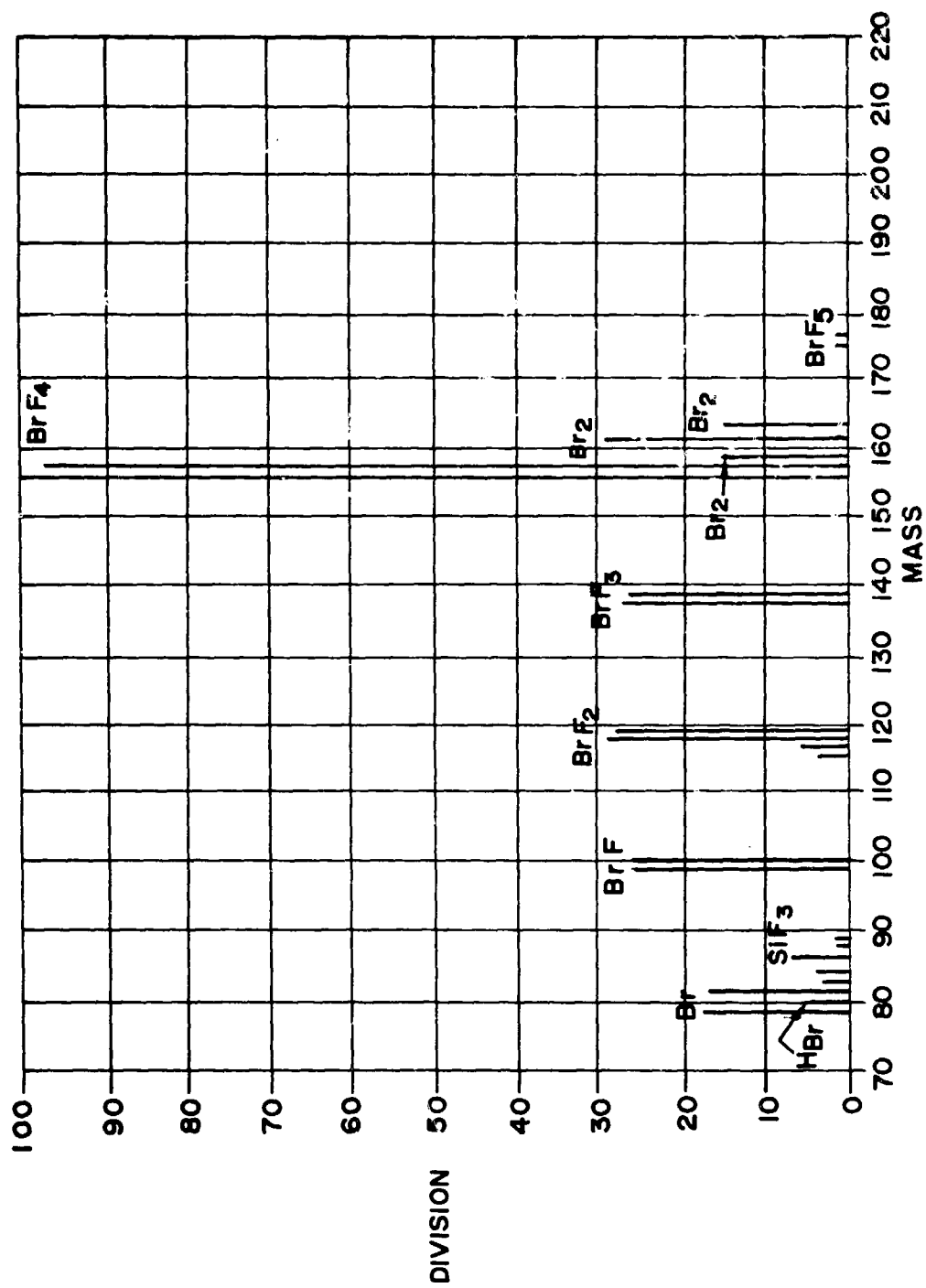
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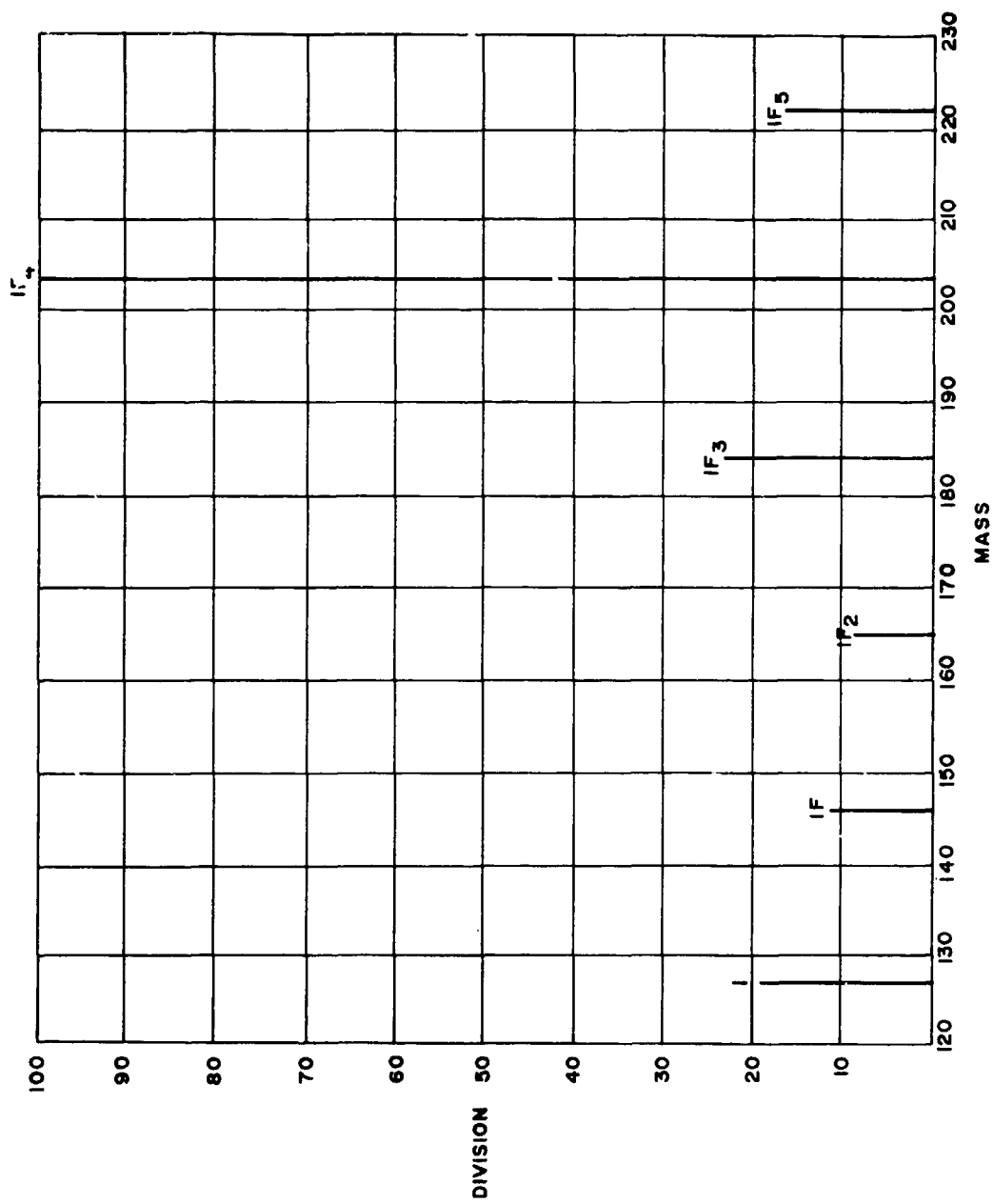


(C) Figure 3. Chlorine Pentafluoride 30 μ a 50 ev

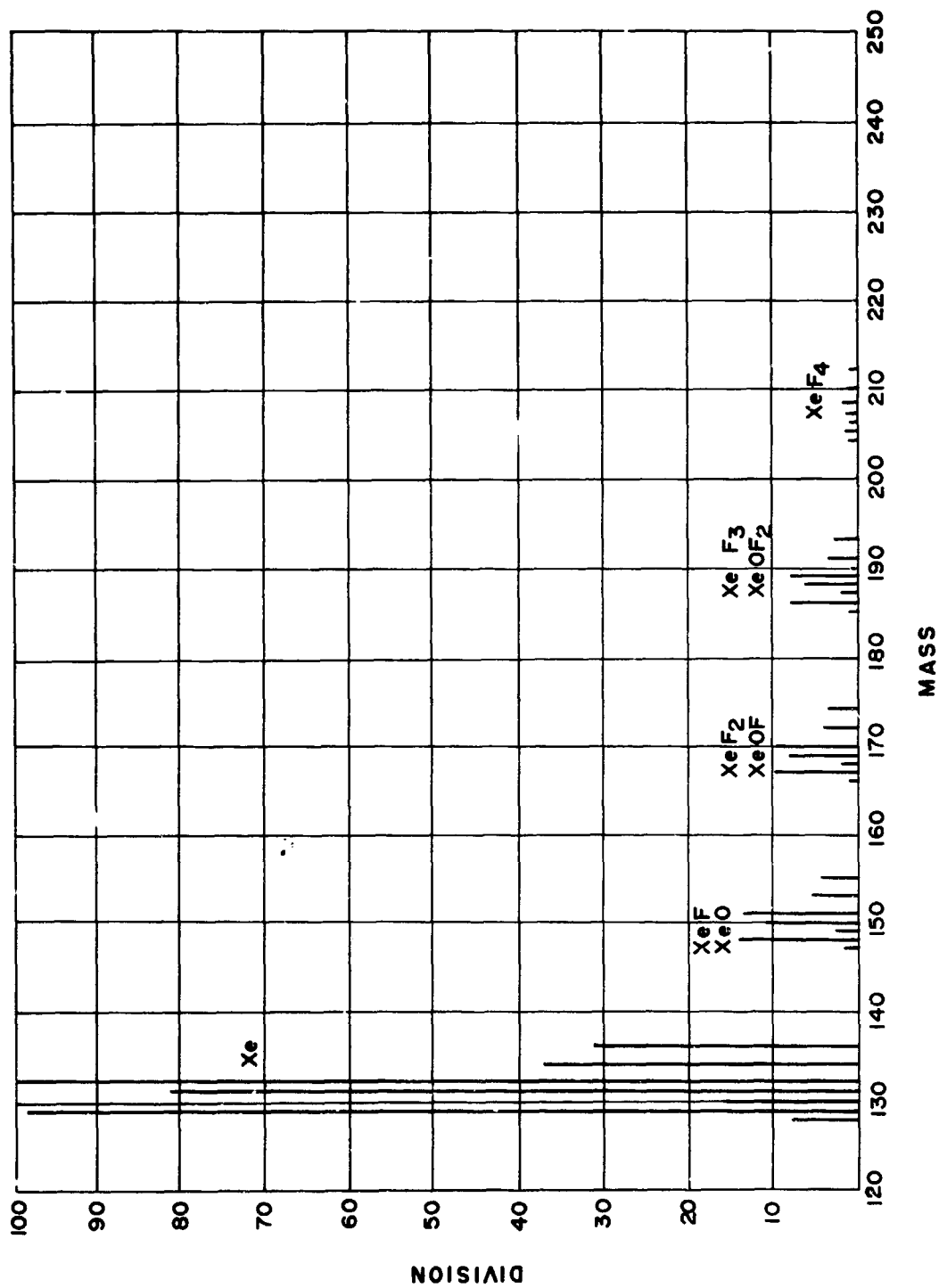
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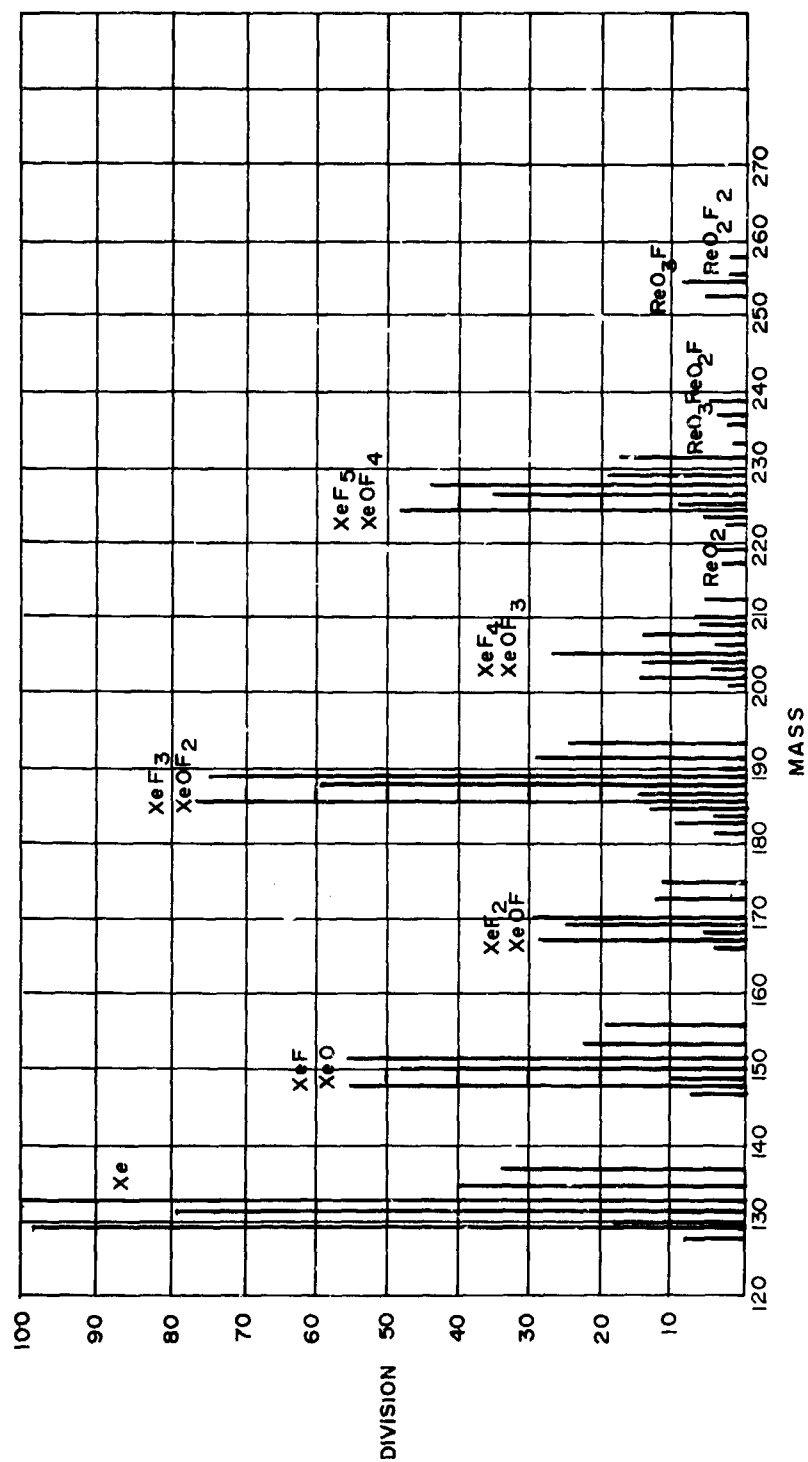
(U) Figure 4. Bromine Pentafluoride ($30\mu\text{a}$ 50 ev)



(U) Figure 5. Iodine Pentafluoride ($30\mu\text{a}$ 50 ev)



(U) Figure 6. Xenon Tetrafluoride ($30\mu\text{a}$ 50 ev)



(U) Figure 7. Xenon Hexafluoride ($30\mu\text{a}$ 50 ev)

(U) The spectra for xenon tetrafluoride and xenon hexafluoride shown in Figures 6 and 7 were at first difficult to obtain. However, little difficulty was encountered after extensive passivation of the manifold with xenon hexafluoride.

(U) The parent molecular ion XeF_4^+ was readily detectable, yet no XeF_6^+ ion corresponding to the xenon hexafluoride parent was detected. Studier and Sloth (3) in their mass spectrometric studies also found the XeF_4^+ parent ion, but did not detect the XeF_6^+ parent ion in normal scans. However, they did detect a small XeF_6^+ parent ion during a high-pressure run. The more probable loss of a fluorine anion from xenon hexafluoride rather than from xenon tetrafluoride may be attributed to the weaker bond of the fluorine atom to the xenon in the xenon hexafluoride. Therefore, it is more probable to see the XeF_4^+ parent ion than the XeF_6^+ parent ion.

(U) The intense ion peaks XeF_5^+ , XeF_3^+ , and XeF^+ in the xenon hexafluoride spectrum, again, result from their stable, even electron configuration. The xenon tetrafluoride spectrum does not show the prominent even-numbered electron ion species. Spectra reported by Svec and Flesch (4) show that the even-numbered electron concept does hold for the xenon tetrafluoride cracking pattern. Apparently, our xenon tetrafluoride decomposed at such a rate that the molecular ions observed did not exhibit the true intensity one would obtain from a cracking pattern of unreacted xenon tetrafluoride.

(U) The ion peaks corresponding to Xe^{129} isotope and fluorine atoms are larger than the isotopic concentration of Xe^{129} relative to Xe^{132} . These ion peaks include ions identified as $\text{Xe}^{132}\text{O}^+$, $\text{Xe}^{132}\text{OF}^+$, $\text{Xe}^{132}\text{OF}_2^+$, and originate from XeOF_2 impurity in the sample. The most intense ion specie, XeOF^+ , has a stable, even-numbered configuration.

(U) The Xe^{129} isotope and fluorine atom ion peaks in xenon hexafluoride are also larger than the isotopic concentration of Xe^{129} .

(U) Ions identified as $\text{Xe}^{132}\text{O}^+$, $\text{Xe}^{132}\text{OF}^+$, $\text{Xe}^{132}\text{OF}_2^+$, $\text{Xe}^{132}\text{OF}_3^+$, $\text{Xe}^{132}\text{OF}_4^+$, contribute to the Xe^{129}F series ion peaks. The even-numbered electronic configuration of XeOF_3^+ is again readily observed by its intense peak.

(U) One would expect to see the parent XeOF type ion species because of the polarizability of xenon, similar to the iodine in the observation of the IF_5^+ parent. Since no ion species corresponding to XeOF_3^+ or XeOF_6^+ were identified, the oxyfluorides in the xenon tetrafluoride and xenon hexafluoride spectra must be XeOF_2 and XeOF_4 . These oxyfluorides may have originated from reactions of the xenon fluorides with oxygen, water vapor, or silicon dioxide (5).

4. CONCLUSIONS.

(U) Modification of the mass spectrometer sample inlet manifold to exclude glass and other potentially reactive materials of construction has proven efficacious for the study of corrosive oxidizers. Reproducible spectra of corrosive gases could be recorded after passivation, indicating that the passivation procedure reported is adequate.

(U) Ion peaks corresponding to impurities like hydrogen fluoride and silicon tetrafluoride in the gases studied were reproducible, showing that this method can be used to identify impurities in corrosive gases with little contribution from products arising from reactions with the mass spectrometer ion source or sample inlet manifold.

(U) The rhenium filament in the ion source used to produce electrons for ion production must be replaced frequently. Rhenium is presently the only filament material available which shows reasonable non-reactivity toward corrosive gases. Nickel appears promising, but has not been investigated.

(U) Mass spectrometric studies of reactive gases can be conducted satisfactorily if resistant materials for the sampling manifold are selected and if appropriate passivation procedures are used.

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1. H. H. Hyman, "Noble Gas Compounds", University of Chicago Press, Chicago, Illinois, p. 36 (1963).
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4. H. J. Svec and G. D. Flesch, Science, Vol. 142, 954 (November 1963).
5. H. H. Hyman, "Noble Gas Compounds", University of Chicago Press, Chicago, Illinois, 1. 106-108 (1963).

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